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(54) Title: BLEACHING COMPOSITION COMPRISING METAL CATALYST, CELLULASE ENZYME, AND OXYGEN BLEACH		
(57) Abstract There is provided a bleaching composition containing an oxygen-releasing bleach system preferably comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound, a metal containing bleach catalyst, preferably a manganese containing bleach catalyst, and a cellulolytic enzyme. The composition is useful in bleachable stain removal particularly when employed in a detergent composition.		

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BLEACHING COMPOSITION COMPRISING METAL CATALYST, CELLULASE ENZYME, AND OXYGEN BLEACH

Technical field

This invention relates to bleaching compositions containing an oxygen-releasing bleach system, a metal containing bleach catalyst and a cellulolytic enzyme for the use in detergent compositions.

Background description

The satisfactory removal of bleachable soils/stains such as tea, fruit juice and coloured vegetable soils from stained fabrics is a particular challenge to the formulator of a bleaching composition for use in a laundry washing method.

Traditionally, the removal of such bleachable stains has been enabled by the use of bleach components such as oxygen bleaches, including hydrogen peroxide and organic peroxyacids. The organic peroxyacids are often obtained by the in situ perhydrolysis reaction between hydrogen peroxide and an organic peroxyacid bleach precursor. More recently, products containing bleach catalysts, particularly manganese bleach catalysts have become of interest.

A problem which is encountered with bleaches containing bleach catalysts in laundry washing methods is the propensity of these bleaches to damage the fabrics being washed. Types of fabric damage can include fading of coloured dyes on the fabrics, or in more extreme cases structural damage to the fibres of the fabric resulting for example, in 'pin-hole' formation in the fabrics.

The Applicants have found that the problem of fabric damage can be reduced by the inclusion of a cellulolytic enzyme into a bleaching composition, employing an oxygen-releasing bleach system and a metal containing bleach catalyst.

It is believed that metal containing catalysts, such as manganese containing catalysts, can damage the fabric by building up of metal containing catalyst upon the fabric. The building up can be caused by interaction of the cationic charge of the catalyst with dyes and anionic charges of cellulose contained in the fabrics or by interaction with the metal containing catalyst already present on the fabric in the washing process.

The Applicants have now found that inclusion of a cellulolytic enzyme, preferably a cellulolytic enzyme, such as the cellulase known as Carezyme (trade name) or an endoglucanase enzyme, in metal catalyst containing detergent compositions can reduce the above mentioned problem. Additionally an amylolytic fungamyl enzyme may be included in the compositions. Also mixtures of different types of cellulolytic enzymes can be used. The mechanism for this reduction in fabric damage is believed to be the action of the cellulolytic enzyme in reducing of the surface area of the fabric and thus the reduction of anionic sites thereon, which can otherwise bind to the metal containing catalyst (such as a manganese catalyst). This leads to a reduction of metal containing catalyst deposition on the fabrics and hence to a reduced propensity to cause fabric damage.

Bleach compositions including a metal containing bleach catalyst, and more specifically a manganese containing bleach catalyst, have been described, for example, in European Patent Applications Nos. EP-A-544,519, EP-A-544,490, EP-A-544,440, EP-A-458,397, EP-A-458,398 and U.S. Patents Nos. US 5,194,416, US 5,246,621 and US 5,244,594. None of these documents disclose the use of a cellulolytic enzymes to inhibit fabric damage associated with the metal containing catalyst or more specifically a manganese bleach catalyst.

Cellulase in the context of compact detergents has been disclosed in WO-92/1305 and EP-A-495257. Cellulase in the context of quaternary ammonium softening compounds has been described in EP-A-495554 and in the context of softening clay in a detergent composition in EP-A-495 258 and EP-A 177165. Cellulase as such has been disclosed in WO 91/17243. EP-A-173397 discloses detergent compositions comprising fungal cellulolytic enzymes. None of these documents disclose the use of a enzyme of the cellulase type to inhibit fabric damage caused by a metal containing bleach catalyst component.

Amylolytic enzymes incorporated in detergent compositions are for example disclosed in JP57028197, GB-1296839 and PCT/US93/06302 and PCT/US93/06877. These documents do not disclose the use of amylolytic enzymes to inhibit damage caused by a metal containing bleach catalyst.

It is an object of the present invention to provide bleaching compositions suitable for use in detergent compositions having good bleachable stain removal wherein the compositions show reduced propensity to cause fabric damage.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

According to the present invention there is provided a bleaching composition comprising

- (a) a oxygen-releasing bleach system;
- (b) a metal containing bleach catalyst ; and
- (c) a cellulolytic enzyme.

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The oxygen-releasing bleach system preferably contains a hydrogen peroxide source and peroxyacid bleach precursor compound.

Preferably the metal containing bleach catalyst is a transition metal containing bleach catalyst, more preferably a manganese containing bleach catalyst, which is most preferably a binuclear complex of manganese, or a manganese gluconate.

Detailed description of the invention

Oxygen releasing bleaching system

An essential feature of the bleach composition of the invention is the inclusion of an oxygen-releasing bleaching system containing an oxygen bleaching species including for example, inorganic perhydrate bleaches or organic peroxyacids.

In a preferred execution the bleaching system contains a hydrogen peroxide source and a peroxyacid bleach precursor compound. The production of the peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the sodium salt at a level of from 1 % to 95 % by weight, more preferably from 10 % to 90 % by weight and most preferably from 20 % to 80 % by weight of the bleaching

compositions. When incorporated in a bleaching composition which is comprised in a detergent composition in accordance with the present invention, the inorganic perhydrate salts are preferably present at a level of from 1 % to 40 % by weight, more preferably from 2 % to 30 % by weight and most preferably from 5 % to 25 % by weight of the detergent composition.

Examples of inorganic perhydrate salts include perborate, perphosphate, persulfate and persilicate salts. A preferred inorganic perhydrate salt is an alkali or alkaline earth metal percarbonate salt.

Sodium percarbonate, which is a preferred percarbonate salt for inclusion in bleach compositions in accordance with the invention, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

Sodium perborate can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilise a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interlox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium

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carbonate which has the general formula $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor compound

Peroxyacid bleach precursors are preferably incorporated at a level of from 1% to 50% by weight, more preferably from 2% to 30% by weight, most preferably from 5% to 20% by weight of the bleaching compositions. When incorporated in a bleaching composition which is comprised in a detergent composition in accordance with the invention, the peroxyacid bleach precursors are preferably present at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight and most preferably from 1.5% to 10% by weight of the detergent composition.

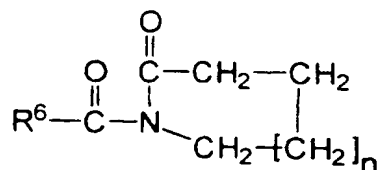
Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

N-acylated lactam precursor compound

N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-855735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

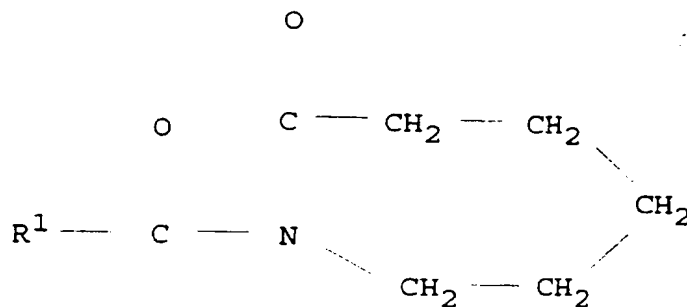
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Suitable N-acylated lactam precursors have the formula:



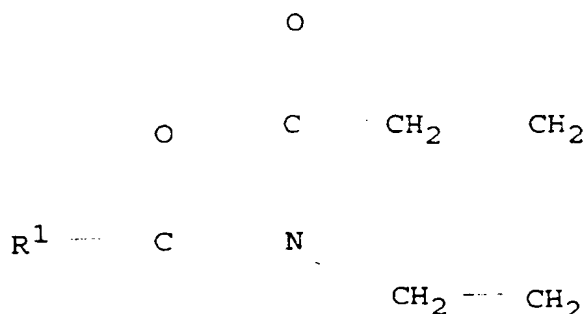
wherein n is from 0 to about 8, preferably from 0 to 2, and R⁶ is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from 6 to 18 carbon atoms

Suitable caprolactam bleach precursors are of the formula:



wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms, most preferably R¹ is phenyl.

Suitable valero lactams have the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at $<30^\circ\text{C}$, particularly the phenyl derivatives, ie. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R^1 moiety contains at least 6, preferably from 6 to 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R^1 comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

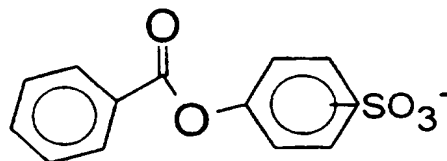
Highly preferred caprolactam and valerolactam precursors include benzoyl caprolactam, nonanoyl capro-lactam, benzoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl caprolactam, 3,5,5-trimethylhexanoyl valerolactam, octanoyl caprolactam, octanoyl valerolactam, decanoyl caprolactam, decanoyl valerolactam, undecenoyl caprolactam, undecenoyl valerolactam, (6-octanamidocaproyl)oxybenzene-sulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-

decanamidocaproyl)-oxybenzenesulfonate, and mixtures thereof. Examples of highly preferred substituted benzoyl lactams include methylbenzoyl caprolactam, methylbenzoyl valerolactam, ethylbenzoyl caprolactam, ethylbenzoyl valerolactam, propylbenzoyl caprolactam, propylbenzoyl valerolactam, isopropylbenzoyl caprolactam, isopropylbenzoyl valerolactam, butylbenzoyl caprolactam, butylbenzoyl valerolactam, tert-butylbenzoyl caprolactam, tert-butylbenzoyl valerolactam, pentylbenzoyl caprolactam, pentylbenzoyl valerolactam, hexylbenzoyl caprolactam, hexylbenzoyl valerolactam, ethoxybenzoyl caprolactam, ethoxybenzoyl valerolactam, propoxybenzoyl caprolactam, propoxybenzoyl valerolactam, isopropoxybenzoyl caprolactam, isopropoxybenzoyl valerolactam, butoxybenzoyl caprolactam, butoxybenzoyl valerolactam, tert-butoxybenzoyl caprolactam, tert-butoxybenzoyl valerolactam, pentoxybenzoyl caprolactam, pentoxybenzoyl valerolactam, hexoxybenzoyl caprolactam, hexoxybenzoyl valerolactam, 2,4,6-trichlorobenzoyl caprolactam, 2,4,6-trichlorobenzoyl valerolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl caprolactam, dimethoxybenzoyl caprolactam, 4-chlorobenzoyl caprolactam, 2,4-dichlorobenzoyl caprolactam, terephthaloyl dicaprolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl valerolactam, dimethoxybenzoyl valerolactam, 4-chlorobenzoyl valerolactam, 2,4-dichlorobenzoyl valerolactam, terephthaloyl divalerylactam, 4-nitrobenzoyl caprolactam, 4-nitrobenzoyl valerolactam, and mixtures thereof.

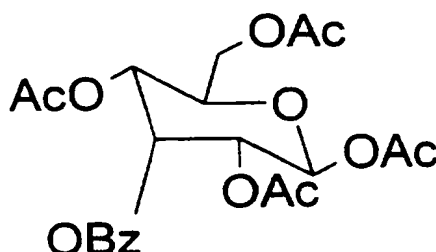
Perbenzoic acid precursor

Essentially any perbenzoic acid precursors are suitable herein, including those of the N-acylated lactam class, which are preferred.

Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



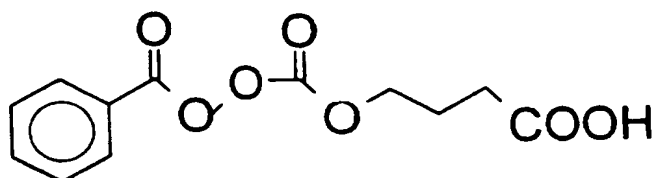
Also suitable are the benzylation products of sorbitol, glucose, and all saccharides with benzylation agents, including for example:



Ac = COCH₃; Bz = Benzoyl

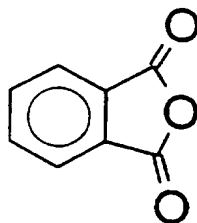
Preferred perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Preferred perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:



Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:

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Perbenzoic acid derivative precursors

Suitable perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the perbenzoic group is substituted by essentially any functional group including alkyl groups.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds are also suitable herein. Typically such cationic peroxyacid precursors are formed by substituting the peroxyacid part with an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group.

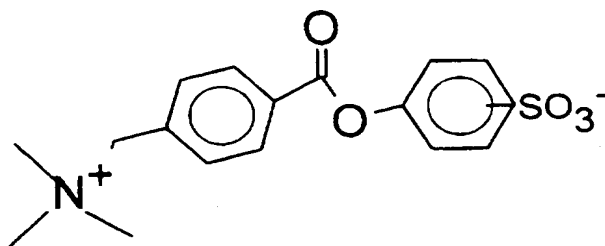
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

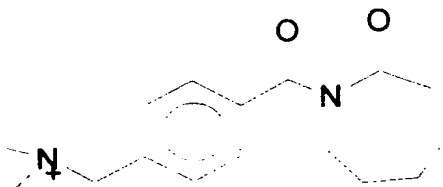
A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:

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A preferred cationically substituted alkyl oxybenzene sulfonate is the methyl ammonium derivative of 2,3,3-tri-methyl hexanoyloxybenzene sulfonate.

Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

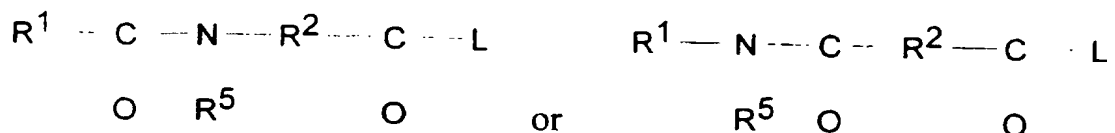
Alkyl fatty peroxyacid bleach precursors

Alkyl fatty peroxyacid bleach precursors form alkyl fatty peroxyacids on perhydrolysis. Preferred precursors of this type give rise to peracetic acid on perhydrolysis.

Preferred alkyl fatty peroxyacid precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Amide substituted peroxyacid bleach precursors

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:

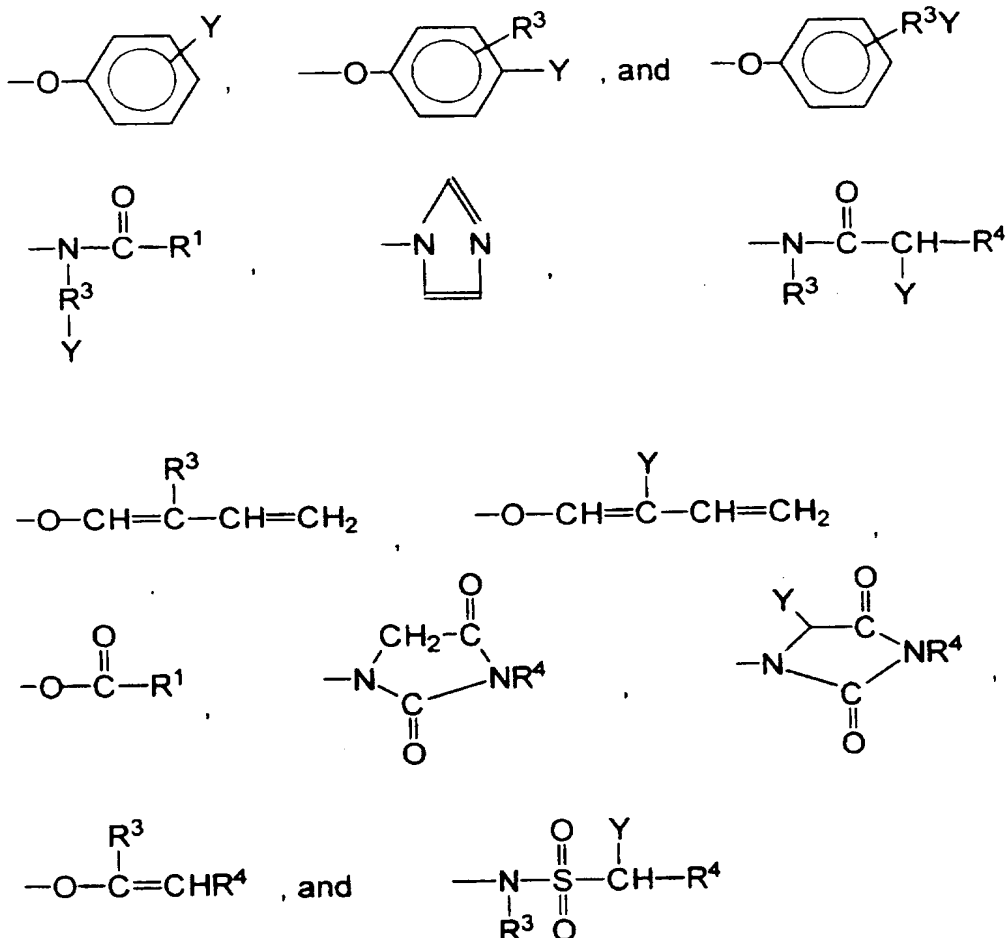


wherein R¹ is an alkyl or aryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from 6 to 12 carbon atoms. R² preferably contains from 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms in total. L may be selected from any of the leaving groups described hereinbefore for the analogues having R¹ as an aryl or alkaryl group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pK_a of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behaviour are those in which their conjugate acid has a pK_a in the range of from 4 to 13, preferably from 6 to 11 and most preferably from 8 to 11.

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Preferred bleach precursors are those wherein R^1 , R^2 and R^5 are as defined for the amide substituted compounds and L is selected from the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group.

The preferred solubilizing groups are $\text{---SO}_3^-\text{M}^+$, $\text{---CO}_2^-\text{M}^+$, $\text{---SO}_4^-\text{M}^+$, $\text{---N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O---N(R}^3)_3$ and most preferably $\text{---SO}_3^-\text{M}^+$ and $\text{---CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide,

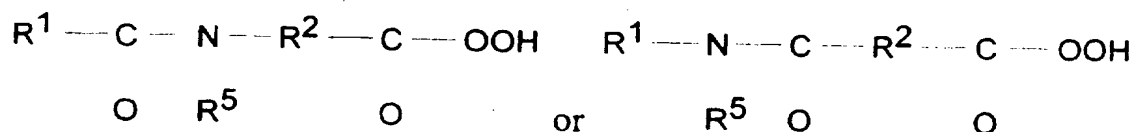
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methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.

Organic peroxyacids

The compositions may contain as components of the bleaching system organic peroxyacids, typically at a level of from 2% to 30% by weight, more preferably from 5% to 20% by weight of the bleaching composition. When the bleaching compositions are comprised in a detergent composition in accordance with the present invention, the organic peroxyacid is preferably present at a level of from 1% to 15% by weight and more preferably from 1% to 10% by weight of the detergent composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R¹ preferably contains from 6 to 12 carbon atoms. R² preferably contains from 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diperoxydodecanedioic acid, diperoxytetradecanedioic acid, diperoxyhexadecanedioic acid, mono- and diperazelaic acid, mono- and diperbrassylic acid.

Metal containing bleach catalyst

The bleach compositions of the invention contain a metal containing bleach catalyst. Preferably the metal containing bleach catalyst is a transition metal containing bleach catalyst, more preferably a manganese containing bleach catalyst and most preferably a bi-nuclear complex of manganese or manganese gluconate.

A suitable type of bleach catalyst is a catalyst comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

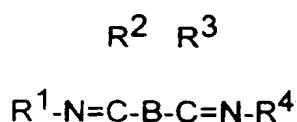
Preferred types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

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The bleach catalysts useful in the compositions herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(\text{OCH}_3)_3\text{-(PF}_6\text{)}$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R^1 , R^2 , R^3 , and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $\text{R}^1\text{-N}=\text{C}-\text{R}^2$ and $\text{R}^3\text{-C}=\text{N}-\text{R}^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR^5R^6 , NR^7 and $\text{C}=\text{O}$, wherein R^5 , R^6 , and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, -bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include $\text{Co}(2,2'\text{-bispyridylamine})\text{Cl}_2$, $\text{Di(isothiocyanato)bispyridylamine-cobalt (II)}$, $\text{tris(dipyridylamine-cobalt(II) perchlorate)}$, $\text{Co}(2,2'\text{-bispyridylamine})_2\text{O}_2\text{ClO}_4$, $\text{Bis-(2,2'-bispyridylamine) copper(II)}$

perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Preferred examples include binuclear Mn complexes with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u-O)_2Mn^{IV}N_4)^+$ and $[Bipy_2Mn^{III}(u-O)_2Mn^{IV}bipy_2]-(ClO_4)_3$.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts) and U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations). Highly preferred catalyst are described U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from

about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a peroxyacid bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Enzyme

The enzyme used in the present invention is a cellulolytic enzyme, that is an enzyme having a cellulolytic activity. Enzymes with amylolytic activity may additionally be included in the bleach composition of the present invention.

Cellulolytic enzyme

Herein the terms "cellulase" and "cellulolytic" denote an enzyme with cellulolytic activity. This means that the enzyme catalyses the hydrolysis of cellulose, and specifically the cellulose fibres of fabric. The cellulolytic enzyme may be a component occurring in a cellulase system produced by a given microorganism, such a cellulase system mostly comprising several different enzyme components including those usually identified as e.g. cellobiohydrolases, exo-cellobiohydrolases, endoglucanases, β -glucosidases.

Alternatively, the cellulolytic enzyme may be a single component, i.e. a component essentially free of other cellulase components usually occurring in a cellulase system produced by a given microorganism, the single component being a recombinant component, i.e. produced by cloning of a DNA sequence encoding the single component and subsequent cell transformed with the DNA sequence and expressed in a host, cf. e.g. International Patent Applications WO 91/17243 and WO 91/17244 which are hereby incorporated by reference. The host is preferably a heterologous

host, but the host may under certain conditions also be the homologous host.

It is contemplated that the cellulolytic enzyme may have an exo-mode of action, the term "exo-mode of action" being intended to mean initiating degradation of cellulose from the non-reducing chain ends by removing cellobiose units.

Alternatively, it is contemplated that the cellulolytic enzyme may have an endo-mode of action, the "endo-mode of action" being intended to mean hydrolysing amorphous regions of low crystallinity in cellulose fibres.

The cellulolytic enzyme herein may be obtained from a microorganism source by use of any suitable technique. For instance, a cellulolytic enzymes preparation may be obtained by fermentation of a microorganism and subsequent isolation of the preparation from the fermented broth or microorganism by methods known in the art, but more preferably by use of recombinant DNA techniques as known in the art. Such method normally comprises cultivation of a host cell transformed with a recombinant DNA vector capable of expressing and carrying a DNA sequence encoding the cellulolytic enzyme in question, in a culture medium under conditions permitting the expression of the enzyme and recovering the enzyme from the culture.

Preferably, the cellulolytic enzyme is a fungal or bacterial cellulase component, i.e. of fungal or bacterial origin.

It is contemplated that the cellulolytic enzyme may be derived or isolated and purified from microorganisms which are known to be capable of producing cellulolytic enzymes, e.g. species of Humicola, Bacillus, Trichoderma, Fusarium, Myceliophthora, Phanerochaete, Schizophyllum, Penicillium, Aspergillus, and Geotricum. The derived components may be either homologous or heterologous components. Preferably, the components are homologous. However, a heterologous component which is immunoreactive with an antibody raised against a highly purified

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cellulolytic enzyme component possessing the desired property or properties and which heterologous component is derived from a specific microorganism is also preferred.

Preferred cellulolytic enzymes herein may be any of those disclosed in the published European Patent Application No. EP-A2-271 004, the cellulolytic enzyme having a non-degrading index (NDI) of not less than 500 and being an alkalophilic cellulolytic enzyme having an optimum pH not less than 7 or whose relative activity at a pH of not less than 8 is 50% or over of the activity under optimum conditions when carboxy methyl cellulose (CMC) is used as a substrate; the cellulolytic enzyme preferably being selected from the group consisting of alkaline cellulase K (produced by Bacillus sp. KSM-635, FERM BP 1485); alkaline cellulase K-534 (produced by Bacillus sp. KSM-534, FERM BP 1508); alkaline cellulase K-539 (produced by Bacillus sp. KSM-539, FERM BP 1509); alkaline cellulase K-577 (produced by Bacillus sp. KSM-577, FERM BP 1510); alkaline cellulase K-521 (produced by Bacillus sp. KSM-521, FERM BP 1507); alkaline cellulase K-580 (produced by Bacillus sp. KSM-580, FERM BP 1511); alkaline cellulase K-588 (produced by Bacillus sp. KSM-588, FERM BP 1513); alkaline cellulase K-597 (produced by Bacillus sp. KSM-597, FERM BP 1514); alkaline cellulase K-522 (produced by Bacillus sp. KSM-522, FERM BP 1512); CMCase I, CMCase II (both produced by Bacillus sp. KSM-635, FERM BP 1485); alkaline cellulase E-II and alkaline cellulase E-III (both produced by Bacillus sp. KSM-522, FERM BP 1512).

A convenient cellulolytic enzyme useful in the bleaching composition of the present invention may be an endoglucanase component which is immunoreactive with an antibody raised against a highly purified ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, or which is a homologue or derivative of the ~43kD endoglucanase exhibiting cellulolytic activity. A preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243, SEQ ID#2, which is shown in the appended SEQ ID NO:4, or a variant of said endoglucanase having an amino acid sequence being at least 60%,

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preferably at least 70%, more preferably 75%, more preferably at least 80%, more preferably 85%, especially at least 90% homologous with said sequence.

Another preferred endoglucanase component comprises an amino acid sequence encoded by the partial DNA sequence disclosed in PCT Patent Application No. WO93/11249; SEQ ID#11, which is shown in the appended SEQ ID NO:5, or a variant of said endoglucanase having an amino acid sequence being at least 60%, preferably at least 70%, more preferably 75%, more preferably at least 80%, more preferably 85%, especially at least 90% homologous with said sequence.

Yet another preferred endoglucanase component comprises an amino acid sequence encoded by the partial DNA sequence disclosed in PCT Patent Application No. WO 93/11249, SEQ ID#9, which is hereby incorporated by reference.

Yet another preferred endoglucanase component comprises an amino acid sequence encoded by the partial DNA sequence disclosed in PCT Patent Application No. WO93/11249, SEQ ID#7, which is hereby incorporated by reference. In example 1 below, the endoglucanase component is referred to as EG III.

Alternatively, the cellulolytic enzyme may be an endoglucanase component which is immunoreactive with an antibody raised against a highly purified ~60kD endoglucanase derived from *Bacillus lautus*, NCIMB 40250, or which is a homologue or derivative of the ~60kD endoglucanase exhibiting cellulase activity. A preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/10732, SEQ ID#7, which is shown in the appended SEQ ID NO:6, or a variant of said endoglucanase having an amino acid sequence being at least 60%, preferably at least 70%, more preferably 75%, more preferably at least 80%, more preferably 85%, especially at least 90% homologous with said sequence.

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The bleaching composition of the present invention should preferably comprise the cellulolytic enzyme at a level of from 0.15% to 10% by weight, more preferably from 0.5% to 6% by weight and most preferably from 1% to 4% by weight of the bleaching composition. When the bleaching composition is comprised in a detergent composition in accordance with the invention, the cellulolytic enzyme is preferably present at a level from of 0.05% to 5% by weight, more preferably from 0.1% to 3% by weight and most preferably from 0.2% to 1.5% by weight of the detergent composition.

Amylolytic enzyme

In the present invention amylolytic enzymes may be included in the bleach composition. Suitable enzymes are amylase enzymes, including endoamylases, for example α -amylases obtained from a special strain of *B. licheniformis* B., described in more detail in GB-1296,839 (Novo). Preferred commercially available amylases include for example Rapidase, sold by BIo-synthetics Inc. and Termamyl, sold by Novo Nordisk A/S. A highly preferred amylase is a fungal species such as amylitic Fungamyl commercially available from Novo Nordisk A/S.

Other suitable amylase enzymes for use herein include Exoamylases, for example β -amylases and χ -amylases derived of vegetable or microbial origin.

Detergent composition

The bleach composition of the invention can be comprised in detergent compositions. The precise nature of the detergent compositions, and levels of incorporation of different components thereof will depend on the physical form of the composition, and the precise nature of the laundering operation for which it is to be used.

The detergent compositions may for example, be formulated as hand and machine laundry detergent compositions, including laundry additive compositions and compositions suitable for use in the pretreatment of stained fabrics.

The detergent composition, comprising the bleach composition of the invention preferably contain one or more additional detergent components selected from surfactants, builders, organic polymeric compounds, additional enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Surfactant

The detergent compositions in accordance with the invention preferably contain as an additional detergent component a surfactant selected from anionic, cationic, nonionic ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

The surfactant is typically present at a level of from 0.1 % to 60 % by weight. More preferred levels of incorporation of surfactant are from 1 % to 35 % by weight, most preferably from 1 % to 20 % by weight.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

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Anionic surfactant

Essentially any anionic surfactants useful for deterative purposes can be included in the compositions. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₆-C₁₈ alkyl sulfates which have been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₆-C₁₈ alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

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Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Anionic carboxylate surfactants suitable for use herein include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Preferred alkyl ethoxy carboxylates for use herein include those with the formula $RO(CH_2CH_2O)_x CH_2COO-M^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C₁₃ or less, and the average x is from about 3 to 10 when the average R is greater than C₁₃, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C₁₂ to C₁₈ alkyl group.

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula

$RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R₁ or R₂ is a succinic acid radical or

hydroxysuccinic acid radical, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Anionic secondary soap surfactant

Preferred soap surfactants are secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should preferably contain no ether linkages, no ester linkages and no hydroxyl groups. There should preferably be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 11-15 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the preferred secondary soap surfactants:

- A. A highly preferred class of secondary soaps comprises the secondary carboxyl materials of the formula $R^3 CH(R^4)COOM$, wherein R^3 is $CH_3(CH_2)_x$ and R^4 is $CH_3(CH_2)_y$, wherein y can be 0 or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of $(x + y)$ is 6-10, preferably 7-9, most preferably 8.
- B. Another preferred class of secondary soaps comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R^5-R^6-COOM , wherein R^5 is C^7-C^{10} , preferably C^8-C^9 , alkyl or alkenyl and R^6 is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note: R^5 can be in the ortho, meta or para position relative to the carboxyl on the ring.)
- C. Still another preferred class of secondary soaps comprises secondary carboxyl compounds of the formula $CH_3(CHR)_k-(CH_2)_m-(CHR)_n-$

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$\text{CH}(\text{COOM})(\text{CHR})_o-(\text{CH}_2)_p-(\text{CHR})_q-\text{CH}_3$, wherein each R is C_1 - C_4 alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion.

Especially preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $\text{R-CON}(\text{R}^1)\text{CH}_2\text{COOM}$, wherein R is a C_5 - C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1 - C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactant

Essentially any anionic surfactants useful for deterative purposes can be included in the detergent compositions in accordance with the present invention. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula $\text{R}^2\text{CONR}^1\text{Z}$ wherein : R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight-chain C_5 -

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C₁₉ alkyl or alkenyl, more preferably straight-chain C₉-C₁₇ alkyl or alkenyl, most preferably straight-chain C₁₁-C₁₇ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C₆-C₁₈ fatty alcohols and C₆-C₁₈ mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C₁₀-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C₁₂-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40.

Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

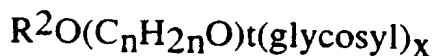
Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be

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substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3; t is from 0 to 10, preferably 0, and x is from 1.3 to 8, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula: $R^6\text{CON}(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

A suitable example of an alkyl amphocarboxylic acid for use herein is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful herein include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 18 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferably 1, ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{18} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10} -18 acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions in accordance with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Betaine surfactant

The betaines useful herein are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group or C₁₀-16 acylamido alkyl group, each R¹ is typically C₁-C₃ alkyl, preferably methyl, and R² is a C₁-C₅ hydrocarbyl group, preferably a C₁-C₃ alkylene group, more preferably a C₁-C₂ alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C₁₂-14 acylamidopropylbetaine; C₈-14 acylamido hexyldiethyl betaine; 4[C₁₄-16 acylmethylamidodiethylammonio]-1-carboxybutane; C₁₆-18 acylamidodimethylbetaine; C₁₂-16 acylamidopentanedithylbetaine; [C₁₂-16 acylmethylamidodimethylbetaine. Preferred betaines are C₁₂-18 dimethyl-ammonio hexanoate and the C₁₀-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Sultaine surfactants

The sultaines useful herein are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-)$ wherein R is a C₆-C₁₈ hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group, more preferably a C₁₂-C₁₃ alkyl group, each R¹ is typically C₁-C₃ alkyl, preferably methyl, and R² is a C₁-C₆ hydrocarbyl group, preferably a C₁-C₃ alkylene or, preferably, hydroxyalkylene group.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions in accordance with the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched.

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Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, silicates and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethoxysuccinates described in British Patent No. 1,379,241,

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lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2.321,001 published on November 15, 1973.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Suitable silicates include the water soluble sodium silicates with an SiO_2 : Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2 : Na_2O ratio of 2.0 is the most preferred silicate.

Silicates are preferably present in the detergent compositions in accord with the invention at a level of from 5% to 50% by weight of the composition, more preferably from 10% to 40% by weight.

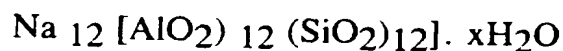
Partially soluble or insoluble builder compound

The detergent compositions in accordance with the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_x[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

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The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite MAP, Zeolite HS and mixtures thereof. Zeolite A has the formula



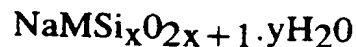
wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Crystalline layered silicate

The detergent compositions in accordance with the invention preferably contains a crystalline layered silicate, preferably present at a level of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition.

The weight ratio of crystalline layered silicate to any peroxyacid bleach precursor compound is preferably from 10:1 to 1:5, more preferably from 5:1 to 1:2, most preferably from 3:1 to 1:1.

Preferred are the crystalline layered sodium silicates having the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

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The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material as described in PCT Patent Application No. WO 92/18594. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof, with citric acid being preferred.

Heavy metal ion sequestrant

The detergent compositions in accordance with the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na₂EDDS and Na₃EDDS. Examples of such preferred magnesium complexes of EDDS include MgEDDS and Mg₂EDDS.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133.

The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS) is also suitable.

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Optional enzymes

The detergent compositions in accordance with the present invention may also comprise one or more optional enzymes.

Preferred optional enzymatic materials include the commercially available lipases, neutral and alkaline proteases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001 % to 4 % active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001 % to 2 % by weight, preferably 0.001 % to 1 % by weight, most preferably from 0.001 % to 0.5 % by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomonas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein.

A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

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Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, but excluding any of the high molecular weight organic polymeric compounds described as flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions in accordance with the invention at a level of from 0.1 % to 30 %, preferably from 0.5 % to 15 %, most preferably from 1 % to 10 % by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

Other suitable organic polymeric compounds include the copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 2,000 to 80,000.

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The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions in accordance with the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01 % to 15 %, preferably from 0.05 % to 10 %, most preferably from 0.1 % to 5 % by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

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Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

Copolymers of ethylene oxide and propylene oxide, particularly the mixed ethoxylated/propoxylated fatty alcohols with an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10, are also suitable antifoam compounds for use herein.

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Suitable 2-alkyl-alcanols antifoam compounds for use herein have been described in DE 40 21 265. The 2-alkyl-alcanols suitable for use herein consist of a C₆ to C₁₆ alkyl chain carrying a terminal hydroxy group, and said alkyl chain is substituted in the a position by a C₁ to C₁₀ alkyl chain. Mixtures of 2-alkyl-alcanols can be used in the compositions according to the present invention.

A preferred suds suppressing system comprises

- (a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination
 - (i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and
 - (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;
- (b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;
- (c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

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A preferred particulate suds suppressor system useful herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica.

The solid silica can be a fumed silica, a precipitated silica or a silica, made by the gel formation technique. The silica particles suitable have an average particle size of from 0.1 to 50 micrometers, preferably from 1 to 20 micrometers and a surface area of at least 50m²/g. These silica particles can be rendered hydrophobic by treating them with dialkylsilyl groups and/or trialkylsilyl groups either bonded directly onto the silica or by means of a silicone resin. It is preferred to employ a silica the particles of which have been rendered hydrophobic with dimethyl and/or trimethyl silyl groups. A preferred particulate antifoam compound for inclusion in the detergent compositions in accordance with the invention suitably contain an amount of silica such that the weight ratio of silica to silicone lies in the range from 1:100 to 3:10, preferably from 1:50 to 1:7.

Another suitable particulate suds suppressing system is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

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Other highly preferred particulate suds suppressing systems are described in copending European Application 91870007.1 in the name of the Procter and Gamble Company which systems comprise silicone antifoam compound, a carrier material, an organic coating material and glycerol at a weight ratio of glycerol : silicone antifoam compound of 1:2 to 3:1. Copending European Application 91201342.0 also discloses highly preferred particulate suds suppressing systems comprising silicone antifoam compound, a carrier material, an organic coating material and crystalline or amorphous aluminosilicate at a weight ratio of aluminosilicate : silicone antifoam compound of 1:3 to 3:1. The preferred carrier material in both of the above described highly preferred granular suds controlling agents is starch.

An exemplary particulate suds suppressing system for use herein is a particulate agglomerate component, made by an agglomeration process, comprising in combination

- (i) from 5% to 30%, preferably from 8% to 15% by weight of the component of silicone antifoam compound, preferably comprising in combination polydimethyl siloxane and silica;
- (ii) from 50% to 90%, preferably from 60% to 80% by weight of the component, of carrier material, preferably starch;
- (iii) from 5% to 30%, preferably from 10% to 20% by weight of the component of agglomerate binder compound, where herein such compound can be any compound, or mixtures thereof typically employed as binders for agglomerates, most preferably said agglomerate binder compound comprises a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 50 to 100; and
- (iv) from 2% to 15%, preferably from 3% to 10%, by weight of C₁₂-C₂₂ hydrogenated fatty acid.

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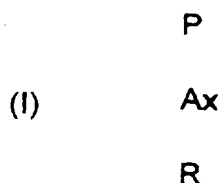
Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01 % to 10 %, preferably from 0.05 % to 0.5 % by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



wherein P is a polymerisable unit, whereto the R-N-O group can be attached to, or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

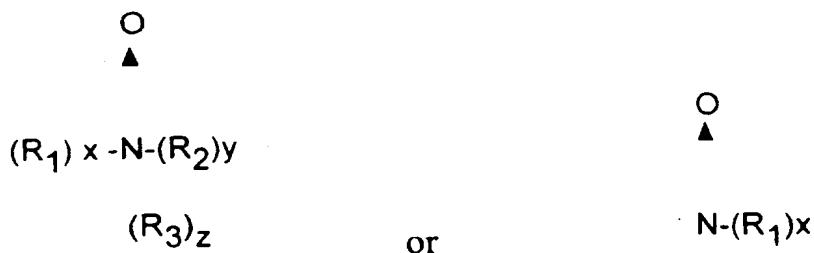


A is NC, CO, C, -O-, -S-, -N-; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :

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wherein R₁, R₂, and R₃ are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

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Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers in the detergent compositions in accordance with the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $\text{PKa} < 10$, preferably $\text{PKa} < 7$, more preferred $\text{PKa} < 6$.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

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b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Preferred polymers for use herein may comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000. The preferred N-vinylimidazole N-vinylpyrrolidone copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

Polyvinylpyrrolidone may be incorporated in the detergent compositions in accordance with the invention at a level of from 0.01% to 5% by weight of the detergent, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylpyrrolidone delivered in the wash solution is preferably from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

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d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylloxazolidone incorporated in the detergent compositions may be from 0.01 % to 5 % by weight, preferably from 0.05 % to 3 % by weight, and more preferably from 0.1 % to 2 % by weight. The amount of polyvinylloxazolidone delivered in the wash solution is typically from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylimidazole incorporated in the detergent compositions may be from 0.01 % to 5 % by weight, preferably from 0.05 % to 3 % by weight, and more preferably from 0.1 % to 2 % by weight. The amount of polyvinylimidazole delivered in the wash solution is from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

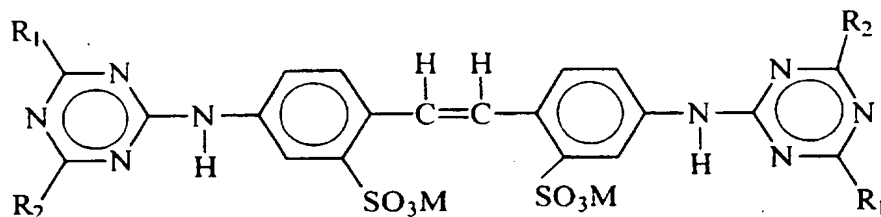
Optical brightener

The detergent compositions herein may also optionally contain from about 0.005 % to 5 % by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the

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compositions herein will preferably comprise from about 0.01 % to 1 % by weight of such optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This

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particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Clay mineral compound

The detergent compositions in accordance with the invention may contain as a fabric softening component a clay mineral compound, preferably present at a level of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition. For

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clarity, it is noted that the term clay mineral, as used herein, excludes sodium aluminosilicate builder compounds.

The weight ratio of clay mineral compound to any peroxyacid bleach precursor compound is preferably from 10:1 to 1:5, more preferably from 5:1 to 1:2, most preferably from 3:1 to 1:1.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$ and the compounds having the general formula $\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites and sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure. Sodium or calcium montmorillonite are particularly preferred.

Suitable smectite clays, particularly montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minerals.

Clays for use herein preferably have a largest particle dimension of from $0.01\mu\text{m}$ to $800\mu\text{m}$, more preferably from 1mm to 400mm , more preferably from 5mm to 200mm .

Particles of the clay mineral compound may be included as components of agglomerate particles containing other detergent compounds. Where

present as such components, the term "largest particle dimension" of the clay mineral compound refers to the largest dimension of the clay mineral compound refers to the largest dimension of the clay mineral component as such and not to the agglomerated particle as a whole.

Substitution of small cations, such as protons, sodium ions, potassium ions, magnesium ions and calcium ions, and of certain organic molecules including those having positively charged functional groups can typically take place within the crystal lattice structure of the smectite clays. A clay may be chosen for its ability to preferentially absorb one cation type, such ability being assessed by measurements of relative ion exchange capacity. The smectite clays suitable herein typically have a cation exchange capacity of at least 50 meq/100g. U.S. Patent No. 3,954,632 describes a method for measurement of cation exchange capacity.

The crystal lattice structure of the clay mineral compounds may have, in a preferred execution, a cationic fabric softening agent substituted therein. Such substituted clays have been termed 'hydrophobically activated' clays. The cationic fabric softening agents are typically present at a weight ratio, cationic fabric softening agent to clay, of from 1:200 to 1:10, preferably from 1:100 to 1:20. Preferred cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These may be present as distinct components or as components of the, hereinbefore described, hydrophobically activated clay materials. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

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Other optional ingredients

Other optional ingredients suitable for inclusion in the detergent compositions in accordance with the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Form of the compositions

The detergent compositions in accordance with the invention can be formulated in any desirable form such as powders, granulates, pastes, and tablets.

Solid compositions

The detergent compositions in accordance with the invention are preferably in the form of solids, such as powders and granules.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1200 g/litre.

Making processes - granular compositions

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

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Laundry washing methods

The compositions in accordance with the invention may be used in essentially any washing or cleaning method, including machine laundry washing methods.

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. The detergent can be added to the wash solution either via the dispenser drawer of the washing machine or by a dispensing device. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred washing method herein a dispensing device containing an effective amount of detergent product is introduced into the drum of a front-loading washing machine before the commencement of the wash cycle.

The dispensing device is a container for the detergent product which is used to deliver the product directly into the drum of the washing machine. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its immersion in the wash water.

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To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use in accord with the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly know as the "granulette".

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

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Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in copending European Application No. 93970141.4.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
C _{xy} E _z S	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7	:	A C ₁₄ -15 predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25E3	:	A C ₁₂ -15 branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5	:	A C ₁₂ -15 branched primary alcohol condensed with an average of 5 moles of ethylene oxide
CEQ	:	R ₁ COOCH ₂ CH ₂ .N ⁺ (CH ₃) ₃ with R ₁ = C ₁₁ -C ₁₃
QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate

- Zeolite A : Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{Al}_{10}\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers
- NaSKS-6 : Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$
- Citric acid : Anhydrous citric acid
- Carbonate : Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm
- Bicarbonate : Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
- Silicate : Amorphous Sodium Silicate ($\text{SiO}_2\text{:Na}_2\text{O}$; 2.0 ratio)
- Sodium sulfate : Anhydrous sodium sulfate
- Citrate : Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm
- MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
- CMC : Sodium carboxymethyl cellulose
- Protease : Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
- Alcalase : Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
- Cellulase : Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
- Amylase : Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
- Lipase : Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase

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- Endolase : Endoglucanase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
- PB4 : Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
- PB1 : Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
- Percarbonate : Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
- NOBS : Nonanoyloxybenzene sulfonate in the form of the sodium salt.
- TAED : Tetraacetythylenediamine
- DTPMP : Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
- Photoactivated : Sulfonated Zinc Phthlocyanine encapsulated in bleach dextrin soluble polymer
- Mn catalyst : $\text{Mn}^{\text{IV}}_2(\text{m-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, as described in U.S. Pat. Nos. 5,246,621 and 5,244,594.
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
- HEDP : 1,1-hydroxyethane diphosphonic acid
- PVNO : Polyvinylpyridine N-oxide
- PVPVI : Copolymer of polyvinylpyrrolidone and vinylimidazole
- SRP 1 : Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
- SRP 2 : Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
- Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

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In the following Examples all levels are quoted as % by weight of the composition:

Example 1

The following laundry detergent compositions A to F were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
CEQ	-	0.8	-	-	0.8	-
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	6.0	6.0	6.0	21.0	21.0	21.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium sulfate	20.1	20.1	20.1	20.1	20.1	20.1
Percarbonate	22.5	22.5	22.5	22.5	22.5	22.5
TAED	1.5	1.5	0.5	0.5	0.5	0.5
Mn Catalyst	0.3	0.2	0.05	0.1	0.3	0.1
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3

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Protease	0.26	0.26	0.26	0.26	0.26	0.26
Cellulase	0.36	0.36	0.36	0.36	0.36	0.36
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100 %						
Density in g/litre	850	850	850	850	850	850

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Example 2

The following granular laundry detergent compositions G to I of bulk density 750 g/litre were prepared in accord with the invention:

	G	H	I
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
CEQ	0.8	2.0	2.0
STPP	15.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	9.8	-	4.3

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Percarbonate	26.0	12.7	10.0
TAED	0.5	3.1	-
Mn Catalyst	0.8	0.5	1.2
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.1	0.1	0.1
Lipase	0.15	0.15	0.15
Cellulase	0.54	1.13	0.28
Amylase	0.1	0.1	0.85
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Perfume	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%			

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Example 3

The following detergent formulations, according to the present invention were prepared, where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent composition:

	J	K	L
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Mn Catalyst	0.4	0.4	0.9
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Cellulase	1.0	1.0	1.0
Lipase	0.4	0.4	0.4

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Amylase	0.25	0.30	0.15
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

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Example 4

The following detergent formulations, according to the present invention were prepared:

	P	Q	R	S
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	20.0	14.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	-	7.5	-	5.0
Bicarbonate	13.0	7.5	10.0	8.0
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.95	0.45	0.4	0.2
Mn Catalyst	0.7	0.45	0.2	1.0
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100

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Example 5

The following detergent formulations, according to the present invention were prepared:

	T	U	V
Blown Powder			
Zeolite A	30.0	22.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	14.0	12.0	22.0
C45AS	8.0	7.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
DTPMP	-	0.4	0.4
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
Mn Catalyst	0.8	0.6	0.5
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Amylase	0.1	0.1	0.1
Cellulase	0.5	0.5	0.5
NOBS	-	6.1	4.5
PB1	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

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Example 6

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodim sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Mn Catalyst	0.01	0.01	0.02
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0

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Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	1.0	1.0	1.0
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

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Example 7

The following high density detergent formulations, according to the present invention were prepared:

	Z	AA
Agglomerate		
C45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
Mn Catalyst	0.3	0.8
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

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WHAT IS CLAIMED IS:

1. A bleaching composition comprising
 - (a) an oxygen-releasing bleach system;
 - (b) a metal containing bleach catalyst; and
 - (c) a cellulolytic enzyme.
2. A bleaching composition according to Claim 1 wherein said oxygen-releasing bleach system comprises a hydrogen peroxide source and a peroxyacid bleach precursor compound.
3. A bleaching composition according to Claim 2 wherein said hydrogen peroxide source is an inorganic perhydrate salt.
4. A bleaching composition according to Claim 3 wherein said inorganic perhydrate salt is present at a level from 1 % to 95 % by weight of the bleaching composition.
5. A bleaching composition according to any of the Claims 2-4 wherein the hydrogen peroxide source is an alkali or alkaline earth metal percarbonate salt.
6. A bleaching composition according to any of the Claims 2 to 5 wherein said peroxyacid bleach precursor compound is present at a level of from 1 % to 50 % by weight of the bleaching composition.
7. A bleaching composition according to any of the preceding Claims wherein said metal containing bleach catalyst is a manganese containing bleach catalyst.

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8. A bleaching composition according to Claim 7 wherein said manganese containing bleach catalyst is a binuclear complex of manganese.
9. A bleaching composition according to Claim 7 wherein the manganese containing bleach catalyst is manganese gluconate.
10. A bleaching composition according to Claim 8 wherein the manganese containing bleach catalyst is $\text{Mn}^{\text{IV}}_2(\text{U-O})_3(1,4,7\text{-trimethyl-1,4,7, triazacyclononane})_2(\text{PF}_6)_2$.
11. A bleaching composition according to any of the preceding Claims comprising an amylolytic enzyme.
12. The use, in a method for washing stained fabrics, of a bleaching composition according to any of the preceding Claims.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/04053

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/395, 386, 02

US CL : 510/305, 309, 310, 311, 312, 320, 374, 378, 392,

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/305, 309, 310, 311, 312, 320, 374, 378, 392,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 5,227,084 A (MARTENS et al) 13 July 1993, see column 2, lines 65-68, column 2, line 1-5, column 4, lines 46-52, column 7, lines 30-32 and 40-50, column 8, lines 53-67.	1-4
Y	US 5,244,594 A (FAVRE et al) 14 September 1993, see col . 2- column 7, lines 53, column 10, lines 30-55, column 12, lines 1-25, column 14, line 34.	1-4
Y	EP 0,544,519 A (HARRIOTT-JUELLER et al) 02 June 1993, see column 3, lines 8-12, column 5, 1-24, column 5, lines 30-32, column 6, lines 1-10, column 7, lines 1-18, column 8, line 39.	1-4
Y	EP 0,544,490, A (MARTENS et al) 02 June 1993, see col 2, lines 1-45, column 4, lines 8-55, column 7, lines 10-11.	1-4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

29 MAY 1997

Date of mailing of the international search report

22 JUL 1997

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/04053

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,246,621 A (FAVRE et al) 21 September 1993, see column 2, lines 40-65, column 11, lines 1-35, column 13, line 40.	1-4

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/04053

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS:

Search terms: cellulase#, cellulolytic, percarbonate#, perborate#, manganese bleach catalyst#